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Diffusion structural diagnostics of polycrystalline boron-doped diamond films

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ABSTRACT

Emanation thermal analysis (ETA) has been used to characterize the thermal behavior of boron-doped diamond polycrystalline film samples prepared by microwave plasma-assisted chemical vapor deposition (MPCVD). The mobility of radon atoms in the diamond film samples was evaluated from the ETA results. From the diffusion structural diagnostics achieved by evaluating the ETA results it followed that the O-plasma treatment of the sample enhanced the mobility of radon atoms in the range of 50–200 °C, due to both structure disordering and removal of graphitic carbon. The structure disordering was suggested by the high-resolution XPS results. From the diffusion structural diagnostics data it followed that the annealing of the structure irregularities in the polycrystalline diamond films took place in the range of 250–450 °C, the annealing was more intense for the O-plasma-treated sample compared to the H-plasma-treated one, due mostly to the initially greater degree of structure irregularities.

1. Introduction

Chemical vapor deposited diamond films are typically treated with hydrogen [1] and oxygen plasmas [2] in order to change the surface termination and to remove non-diamond carbon impurities. Although much information has already been obtained about the effects of such treatments, there is still a need for more detailed structural information at the atomic level, for example, the degree of disordering, and, even more importantly, the effect of thermal treatments that can relieve the plasma-induced disordering.

In the present work, the emanation thermal analysis (ETA) technique [3] was used to characterize the thermal behavior of boron-doped polycrystalline diamond films (thickness of the order of several tens of nanometers, i.e. up to 200 atomic layers) prepared by microwave plasma-assisted chemical vapor deposition (MPCVD) and to reveal the effect of the subsequent treatment using an oxygen plasma. In this technique, radon atoms were implanted into the diamond surface and their diffusion was investigated under *in situ* conditions during the thermal treatment of the samples. The radon release rate measured was used to assess their mobility along structural irregularities serving as radon diffusion paths, and consequently the thermal annealing of these paths could be characterized from the ETA results. A mathematical model of the radon diffusion in the heterogeneous solid was designed and used in the diffusion structural diagnostics of the samples. The chemical state of the surfaces of the samples was characterized by X-ray photoelectron spectroscopy (XPS), which also provided support for the disordering effect of the oxygen plasma.

Diamond layers can be grown by using various techniques. In the MPCVD technique [4,5], it is well known that diamond films prepared from the gas phase are strongly affected by the synthesis conditions. The diamond surface has to be stabilized by hydrogen plasma treatment. Atomic hydrogen has several critical roles, namely, stabilization of the diamond surface, generation of condensable carbon radicals in the gas, production of vacant surface sites, and etching of graphite [4]. The main effects of hydrogen plasma treatment after the initial deposition include the production of a fully H-terminated surface, e.g., a 2×1 type termination on the (1 0 0) surface [6,7], as well as the production of a subsurface region, extending several nm or more, in which hydrogen is actually incorporated into the solid structure [8–11].

There are various types of oxidative treatments available, including chemical, electrochemical and oxygen plasma [12]. The latter is attractive, because it is a rapid, convenient, easily controllable, dry-type technique. It can both change the surface termination, to a monolayer of chemically bound oxygen [13,14], as well as remove graphitic carbon from the surface or from grain boundaries. In addition, oxygen plasma etching is a powerful tool in micromachining diamond [15–20]. However, due to the high kinetic energy of the oxygen ions and/or power (e.g., 100 W, 13.56 MHz, 0.88 W cm^{-2} [21]), some structural disorder can also be introduced.

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Therefore, it was of interest to not only study the chemical state of the surface but also to characterize the samples after the respective plasma treatments by using the diffusion structural diagnostics. The information obtained from the latter technique can be used in the production of diamond films with reproducible characteristics for electronic devices, electrochemical sensors and other applications.

Diffusion structural diagnostics of solids consists in the characterization of diffusion properties of solid samples by using inert gases as tracers. Changes in surface morphology and microstructure of the solid samples during thermal treatments and changes due to chemical, mechanical or radiation interactions can be studied by the technique of diffusion structural diagnostics. The emanation thermal analysis, based on the measurement of the release of radon atoms from the solids, was used [22] in the diffusion structure diagnostics of the samples.

2. Experimental

2.1. Preparation of samples

Polycrystalline boron-doped diamond thin films were grown by the microwave plasma-assisted chemical vapor deposition (MPCVD) method using a commercial microwave plasma reactor (Seki Technotron Corp., Tokyo, Japan, formerly ASTeX Corp., Woburn, MA, USA). Details of the deposition process have been reported elsewhere [24]. The films were grown on Si (1 0 0) substrates having a thickness of 0.6 mm. A mixture of acetone and methanol (9:1 volume ratio) was used as the carbon source. B_2O_3 (B/C at. ratio, 10 ppm) was dissolved in the solvent mixture. High purity hydrogen was used as the carrier gas. Freestanding films with thickness of approx. 40 μm were obtained after etching the Si substrates in a mixture of HF and HNO_3 (55% HF, 61% HNO_3, mixed 2:1, v/v). The samples thus obtained were treated with a hydrogen plasma at a power of 1 kW for 5 min in order to achieve a maximum hydrogen termination. The film quality was confirmed by the presence of the sharp characteristic Raman spectroscopy peak at 1332 cm^{-1}.

After the above procedure, the samples are referred to as "H-plasma-treated." One of these samples was subsequently treated in an oxygen plasma (Samco Co., FA-1) at 20.0 Pa at 70 W for 5 min in order to convert the hydrogen termination to oxygen. This sample is referred to as "O-plasma-treated."

2.2. Emanation thermal analysis as a tool for diffusion structural diagnostics

The ^{220}Rn atoms were used as a microstructure probe incorporated into the samples by using the recoil energy (85 keV/atom), which was gained by a spontaneous α-decay according to the scheme.

$$^{228}\mathrm{Th} \xrightarrow[T_{1/2}=1.9\,\mathrm{y}]{\alpha} {}^{224}\mathrm{Ra} \xrightarrow[T_{1/2}=3.8\,\mathrm{d}]{\alpha} {}^{220}\mathrm{Rh} \xrightarrow[T_{1/2}=55.9\ \mathrm{s}]{\alpha} \quad (1)$$

The thorium nuclide ^{228}Th (half-life 1.9 years) served as a quasi-permanent source of radon ^{220}Rn (half-life 55 s). The half-life of ^{220}Rn ensured that a steady state between ^{224}Ra and ^{220}Rn was established within several minutes.

It has been supposed that the ^{220}Rn and ^{224}Ra atoms are trapped on lattice defects. It has been assumed that the defects, such as vacancy clusters, grain boundaries and other structural irregularities, served as diffusion paths for the radon atoms [22]. The recoil of radon atoms from the sample surface was taken into account in addition to the radon diffusion.

The release rate of radon from the sample, also called the radon release rate, E, can be expressed in a simplified way as follows:

$$E = E_{\mathrm{Recoil}} + E_{\mathrm{Diffusion}} = E_{\mathrm{Recoil}} + D(T) \cdot \Psi(T) \quad (2)$$

where E_{Recoil} is the radon release rate due to recoil, depending on the external surface area, $E_{\mathrm{Diffusion}}$ is rate of the radon release rate due to diffusion, depending on the number of radon diffusion paths, D is the radon diffusion coefficient in the solid: $D = D_0 \exp(-Q/RT)$, where D_0 is a pre-exponential factor, Q is the activation energy for radon diffusion, and T is the temperature in Kelvin. The function $\Psi(T)$ is proposed for the description of the change of number of defects, which served as radon diffusion paths.

2.3. Labeling of samples for ETA

The samples for ETA measurements were labeled using absorption of ^{228}Th and ^{224}Ra radio-nuclides from acetone solution. The specific activity of the sample was 10^5 Bq per gram. The labeled samples were stored three weeks prior to the ETA measurements under dry conditions in air to allow the radioactive equilibrium between the ^{228}Th and ^{224}Ra nuclides to be established.

The recoil depths of the ^{224}Ra and ^{220}Rn ions implanted by the recoil energy (85 keV/atom) into diamond (density, 3.51 g/cm^3) were calculated by means of the TRIM code [23] as follows: for ^{224}Ra, the recoil depth is 21.1 nm (straggling, 2.7 nm), and for ^{220}Rn, the recoil depth is 21.1 nm (straggling, 3.1 nm). Therefore, we supposed that the radon atoms penetrated into the diamond near-surface layers to a maximum depth of ca. 48.0 nm.

In the ETA measurements the samples were placed into a corundum crucible and heated in argon at a heating rate 6 K/min rate from 20 to 450 °C and subsequently cooled at the same rate to room temperature. The rate of radon release from the sample was measured under *in situ* heating conditions.

The constant flow of the argon (flow rate 50.0 mL/min) served to transport the radon released from the sample into the chamber in which the radon radioactivity was measured. The ETA results are presented as temperature dependences of radon release rate E (in relative units); $E = A_\alpha/A_{\mathrm{total}}$, where A_α is the α-radioactivity of radon released per unit time from the labeled sample, and A_{total} is the total γ-radioactivity of the labeled sample.

The A_{total} value is proportional to the rate of radon formation in the sample. Semiconductor and NaI(Tl) detectors were used for the α- and γ-radioactivity measurements, respectively.

2.4. X-ray photoelectron spectroscopy (XPS)

XPS measurements were carried out using a PHI Model 5600 (Perkin-Elmer) spectrometer fitted with a monochromator using Mg Kα radiation (400 W) at a pass energy of 58.7 eV. There was negligible contribution to the spectra due either to the exposure of the samples to the atmosphere or to impurities present in the spectrometer itself.

3. Results

The mobility of radon atoms in the boron-doped diamond film samples in the temperature range of 50–200 °C due to the presence of defects and structure irregularities and the annealing thereof occurring in the range of 250–450 °C, were evaluated from the ETA results. Fig. 1 shows the ETA results of the H-plasma-treated sample (curve 1) and the O-plasma-treated sample (curve 2). We suppose that the increase of the radon release rate, E, observed in both curves 1 and 2 in the range of 20–150 °C is controlled by the single-jump diffusion mechanism. During heating in this temperature range, radon atoms escaped from the traps and diffused to the sample